

First Quarterly Progress Report
26 Jan. 1978

**CHEMICAL COMPOSITION AND PROCESSING
SPECIFICATIONS FOR AIR FORCE
ADVANCED COMPOSITE
MATRIX MATERIALS**

Contract F33615-77-C-5196

AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

GRUMMAN AEROSPACE CORPORATION
BETHPAGE, NEW YORK 11714

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FOREWORD

The work reported herein was performed under the sponsorship of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433. Dr. Charles E. Browning, AFML/MBC is the Air Force Project Engineer.


The work was performed by the Materials and Processes Department of the Grumman Aerospace Corporation, Bethpage, New York. The Industrial Systems Department, Hercules Incorporated, Magna, Utah, and AVCO Systems Division, Lowell, Massachusetts, are subcontractors for this program. Key Grumman personnel associated with the program and their areas of responsibility are:

H. Borstell	Project Engineer
R. Holden	Chemical Analysis
P. Donohue	Element Test

The Project Engineers for Hercules and AVCO are Dr. R. E. Hoffman and R. Loszewski, respectively.

This report has been approved by:


H. Borstell
Project Engineer


C. Micillo
Manager, Advanced Materials and
Process Development

Section 1

INTRODUCTION AND SUMMARY

1.1 INTRODUCTION

1.1.1 Background

Advanced composite structures for production aircraft manufactured over an extended time span must be made from prepregs having uniformly consistent matrix resins to ensure the reliability, reproducibility, and durability of the composite structures. Possible variations in the matrix systems can occur due to changes in the purity and concentration of the various ingredients and their processing. These variations may not be detected by laminate and prepreg testing required by current material procurement specifications. However, a variety of analytical methods are currently available to characterize or "fingerprint" resin systems. Thus, improved reliability and reproducibility of advanced composite prepreg materials can be realized by expanding existing material procurement specifications to include chemical composition and processing specifications for the matrix systems.

1.1.2 Program Objective

The objective of this program is to develop, establish, and implement compositional and processing specifications for advanced composite matrix materials used on Air Force weapons systems. The specific materials to be studied under this program are the Hercules 3501-5A/A-S graphite/epoxy and AVCO 5505 boron/epoxy prepregs.

1.1.3 Program Plan

The two advanced composite matrix systems will be studied under separate tasks using the task flow diagram shown in Figure 1. Resin batches with known variations in purity, concentration, processing (or combinations thereof) will be prepared and converted into prepregs using production facilities. The variations were selected on the basis of anomalies which could occur even though they might be detected by the prepreggers existing Quality Control network. The various prepreg batches will be subjected to the receiving/shipping inspections required by the applicable material specifications. These data will highlight any variations early in the program that

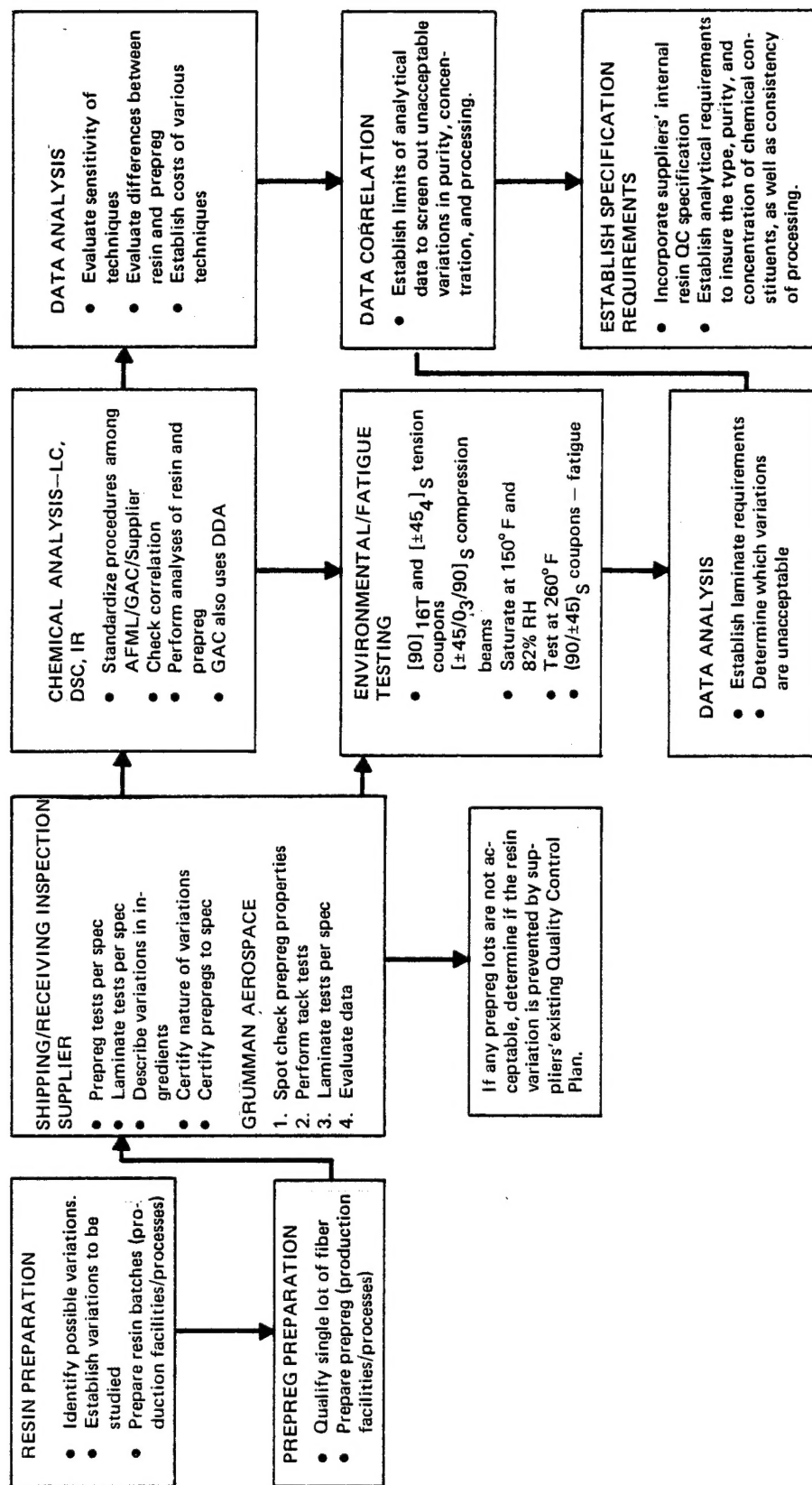


Figure 1 Program Task Flow Diagram

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result in rejectible prepregs so that suitable precautions can be taken, if required. Then, the resin and prepreg will be subjected to chemical analysis using standardized techniques. The techniques will include Liquid Chromatography (LC), Differential Scanning Colorimetry (DSC), Infra-Red Spectroscopy (IR), and Dynamic Dielectric Analysis (DDA). The various techniques will be evaluated for sensitivity, accuracy and cost. Concurrently, laminate properties after humidity exposure at 150°F and 82 percent RH and fatigue loading at ambient conditions will be determined. The laminate data will then be compared to design allowables to determine which variations are structurally unacceptable. The analytical data and laminate data will be correlated to establish limits for acceptable resin variations. Thus, the effects of matrix variations on laminate properties will be established and the analytical data used to reject resin or prepreg batches that have variations adversely affecting the durability of composite structures. The chemical composition and matrix processing requirements will then be incorporated into the applicable material specifications.

1.2 SUMMARY

1.2.1 Program Schedule

The schedule for this two-task program is shown in Figure 2. The technical effort, including preparation of the final report draft, will be completed in 16 months. Due to the critical nature of the program, a reasonable effort will be made to accelerate the schedule so that these data become available more rapidly.

1.2.2 Work Accomplished to Date

Task I: Hercules 3501-5A/A-S Graphite/Epoxy

- Prepared resin batches and derived prepreg
- Selected basic analytical techniques
- Started shipping/receiving inspection

Task II: AVCO 5505-4 Boron/Epoxy

- Prepared resin batches
- Preparation of prepreg is 75 percent complete

1.2.3 Program Status

All tasks are on schedule.

Section 2

TASK I: HERCULES 3501-5A/A-S GRAPHITE/EPOXY

2.1 PRODUCTION OF RESIN BATCHES AND PREPREG

The 3501-5A resin system contains a minimum number of ingredients and is formulated to provide consistency in resin processing and shop handling. Thus, no variations in resin processing were considered necessary for this program. Nine variations were selected to reflect possible changes in the purity and concentration of the various components: Figure 3. The low viscosity base resin variation was made from material having a viscosity level 12 percent below the minimum acceptable value. The high viscosity base resin variation was prepared from base resin that met Hercules requirements but is the highest viscosity material available. The brittle and ductile resins represent worst possible cases and were produced by using off-grade base resins and variations in both hardener and accelerator content. The variations were produced in subscale batches with a standard subscale batch for control purposes. Production facilities and processes were used to produce the subscale batches. Resin from a full-scale production batch was included to identify the effects of scale up.

Twelve-inch wide prepreg was prepared from a single lot of A-S1 fiber using the production tape line. Samples of the various resin batches and derived prepreg were delivered to both Grumman and AFML on 14 December, 1977.

1. HIGH-VISCOSITY BASE RESIN
2. LOW-VISCOSITY BASE RESIN
3. BRITTLE RESIN
4. DUCTILE RESIN
5. INCREASED ACCELERATOR MOISTURE CONTENT
6. HARDENER CONCENTRATION - 10% EXCESS
7. HARDENER CONCENTRATION - 10% BELOW NORMAL
8. ACCELERATOR CONCENTRATION - 20% EXCESS
9. ACCELERATOR CONCENTRATION - 20% BELOW NORMAL
10. STANDARD SUBSCALE BATCH
11. STANDARD PRODUCTION BATCH

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Figure 3 Hercules 3501-5A Resin Variations

2.2 SHIPPING/RECEIVING INSPECTION

Grumman and Hercules will perform the testing required to qualify all 11 batches of prepreg to the requirements of Grumman Specification GM 3013, "Graphite-Reinforced, Epoxy Preimpregnated Material, Low Pressure Molding."

Prepreg physical properties being measured by Hercules include volatile and resin contents and fiber areal weight. Grumman tack testing has demonstrated that all batches have adequate tack after five days exposure at room temperature. All batches have adequate adhesion to a layup template after 14 days.

The unidirectional laminate properties to be measured by both Hercules and Grumman include:

- Flexural strength and modulus at 75°F and 350°F
- Horizontal shear strength and modulus at 75°F and 350°F
- Tensile strength and modulus at 75°F.

The test laminates were cured using the cycle shown below. This task will be completed during the next reporting period.

The curing procedure shall be as follows:

1. Draw 20 in. (508mm) Hg. (min.) vacuum on bagged part and place in autoclave.
2. Apply 85 ±5 psi (586 ±35kPa) pressure. Turn vacuum off and check the bag for leakage. The vacuum level shall not fall to 10 in. (254mm) of Hg. in 2 minutes or less. If bag fails test, remove part from autoclave, repair bagging defect and repeat steps 1 and 2.
3. If bag passes leak check, re-establish 20 in. (508mm) Hg. (min.) vacuum to part and reduce autoclave pressure to 0.
4. Heat part from 120°F(49°C) to 225°F(107°C) in 60 ±15 minutes maintaining 20 in. (508mm) Hg. minimum vacuum on part.
5. When part reaches 225°F (107°C), pressurize autoclave to 85 ±5 psi (586 ±35 kPa).

6. Hold at 225 ± 10 , -0°F ($107 + 6$, -0°C) 85 ± 5 psi (586 ± 35 kPa) pressure and 20 in. (508mm) Hg. vacuum for 50 to 60 minutes.
7. Reduce vacuum to 2 in. (50.8mm) of Hg. maximum. Raise part temperature to $350 \pm 10^{\circ}\text{F}$ ($177 + 6^{\circ}\text{C}$) in 60 ± 15 minutes.
8. Hold at $350 \pm 10^{\circ}\text{F}$ ($177 \pm 6^{\circ}\text{C}$), 85 ± 5 psi (586 ± 35 kPa) pressure and 2 in. (50.8mm) Hg. maximum vacuum for 60 ± 5 minutes.
9. Cool laminate to 250°F (121°C) at a continuous rate of less than 1°F (0.6°C) per minute. Then cool laminate to 150°F (66°C) in not less than 80 minutes (approx 1.3°F (0.7°C) per minute, maximum).
10. Remove bag and all bleeders and post cure part in an oven at $340 \pm 10^{\circ}\text{F}$ ($171 \pm 6^{\circ}\text{C}$) for $8 + 0.5$, -0 hours. Heat parts from 120°F (49°C) to $350 + 0$, -20°F ($177 + 0$, -11°C) in not less than 60 minutes. After post cure, cool parts to 250°F (121°C) in not less than 30 minutes.

2.3 CHEMICAL ANALYSIS

The basic chemical analysis techniques for the 3501-5A resin system were developed under an AFML-sponsored round robin involving various industry and government agencies. The various test procedures are reported in the footnote below. In addition, Hercules has also developed analytical procedures that are applicable to this program. The basic analytical techniques to be used have been selected. However, minor refinements and standardization of techniques will be made during on-site visits to both laboratories. Hercules will analyze the neat resins only by LC, DSC, and IR so that confidence in the resin can be obtained prior to committing the resin to the prepreg operation. Grumman will analyze both resin and prepreg using LC, DSC, IR, and DDA.

NOTE: Chemical Quality Assurance Test Procedures for Advanced Composite Resin Matrices, D.K. Hadad, et al, Lockheed Missile and Space Company, Inc., July 1977.

Section 3

TASK II: AVCO 5505-4 BORON/EPOXY

3.1 PRODUCTION OF RESIN BATCHES AND PREPREG

The 5505 resin system is a complex formulation with numerous possible variations in concentration and purity. Previous Grumman production experience with this prepreg has also shown that variations in the reactivity of the resin and tack of the prepreg have occurred. Thus, the 14 variations shown in Figure 4 were selected for study under this program. The very brittle and low modulus batches represent worst cases and were prepared by varying the concentration and/or purity of several ingredients. The variations in hardener particle size and moisture content, and time/temperature history were selected to determine the effect of variations in the reactivity of the resin on structural durability.

The various resin batches were prepared in production facilities in sufficient quantities to insure a reasonable correlation with the mixing of larger full-scale production resin batches. The subscale standard batch is included as a control.

1. COARSE PARTICLE SIZE CURING AGENT-NORMAL CONCENTRATION
2. FINE PARTICLE SIZE CURING AGENT-NORMAL CONCENTRATION
3. HIGH MOISTURE CONTENT CURING AGENT
4. COMPONENT A-1 - 10% EXCESS
5. COMPONENT A-1 - 10% BELOW NORMAL
6. COMPONENT A-2 - 10% EXCESS
7. COMPONENT A-2 - 10% BELOW NORMAL
8. IMPURE COMPONENT B - NORMAL CONCENTRATION
9. COMPONENT C - 10% EXCESS
10. COMPONENT C - 10% BELOW NORMAL
11. VERY BRITTLE BATCH
12. LOW-MODULUS BATCH
13. SLOW HEAT-UP TO MIXING TEMPERATURE
14. SLOW HEAT-UP TO MIXING TEMPERATURE AND SLOW COOL DOWN
15. SUBSCALE STANDARD BATCH
16. STANDARD PRODUCTION BATCH

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Figure 4 AVCO 5505-4 Resin Variations

The AVCO 5505-4 boron/epoxy prepreg contains a style 104 glass carrier to facilitate layup. The prepreg prepared for this program will contain custom-made scrim cloth impregnated with the same resin used to prepreg the boron fibers. Thus, only one resin batch will be used in each experimental lot of prepreg to simplify understanding the chemical analytical data. This task was scheduled to be completed on January 31, 1977.

3.2 CHEMICAL ANALYSIS

Due to the complexity of the 5505 resin system, the specific analytic procedures to be used in this task cannot be selected at present. During the next reporting period, the available technology base will be assessed to assist in the preliminary selection of analytical techniques.